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Jiacai Wang^a; Zuoying Xue^a

^a Chinese PLA Jinan General Hospital, Jinan, P. R. China

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ADSORPTION OF PYRIDINE DERIVATIVE ON SILVER SURFACE

Keywords: Fourier transform Surface Enhanced Raman Scattering spectroscopy (FT-SERS), milrinone injection, adsorption, silver surface

Jiacai Wang*, Zuoying Xue

Chinese PLA Jinan General Hospital, Jinan, 250031, P. R. China

ABSTRACT The Chemisorption and conformation of milrinone injection on HNO_3 etched silver foil and chemically reduced silver films have been investigated by Fourier transform Surface Enhanced Raman Scattering spectroscopy (FT-SERS).

INTRODUCTION

Organic nitrogen compounds can coordinate strongly to some metal surface and form monomolecular films¹, which is well-organized microscopic characteristic and endows the metals attached many special properties. This is of great significance in the composite, especially in the application of artificial bones and organs. Due to its very high spectral resolution and excellent sensitivity, SERS become an impetus to the interfacial science ^{2,3}.

* Corresponding author

Now FT-Raman spectrometer has found wide application in the drug and tissue analysis ^{4,5}. In this paper we used it to study the chemisorption of milrinone injection on silver surface.

EXPERIMENTAL

Milrinone injection was supplied by Lunan Pharmacy Co. China. All other chemicals were analytical reagent. In a 10 ml beaker were a few of 10×10×1 mm glass plates, which had been washed with water and acetone. 5 ml 0.2 M silver ammonia complex and 5 ml 5% formaldehyde aqueous solution were mixed in the beaker. Several seconds later the solution turned to gray. Meanwhile the silver ions were reduced and deposited on the glass plates to form fine silver films ⁶. After withdrawing the plates covered with silver were washed with distilled water and then dipped in 1mg/ml milrinone aqueous solution for five minutes. The treated samples were washed with water and ready for FT-SERS spectrum measurement. The samples on HNO₃ etched silver foils were prepared according to the procedure described previously⁷. FT-Raman spectra were recorded with a Bruker model RFS 100 Fourier Raman spectrometer with an air-cooled diode pumped Nd-YAG laser and Ge-detector, which operates at liquid nitrogen temperature. The incident laser line was 1064 nm and the resolution was 4.0 cm⁻¹. The outputs were 250 mW for solid milrinone solid and samples on the chemically reduced silver film. The output was 30 mW for the samples on HNO₃ etched silver surface.

RESULTS AND DISCUSSION

Organic nitrogen compounds are easily chemisorbed on silver or gold surface with nitrogen ¹. FIG.1 represents the molecular structure of milrinone. FIG. 2 shows the spectra of milrinone solid(a) and its FT-SERS on the chemically reduced silver film (b) and HNO₃ etched silver foil. The bands at

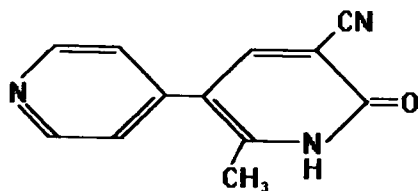


FIG. 1 Molecular structure of milrinone

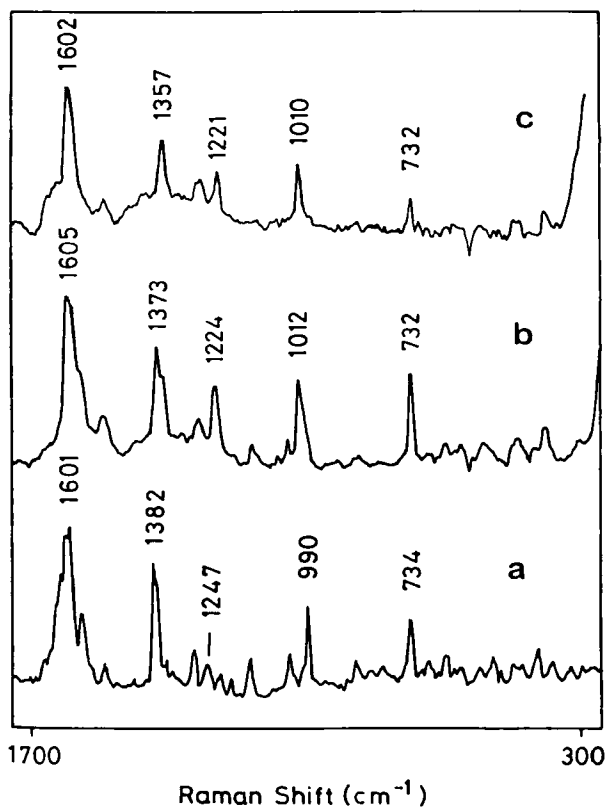


FIG. 2 FT-Raman spectra of milrinone (a) and its FT-SERS spectra after adsorption on chemically reduced silver surface (b) and on HNO₃ etched silver surface (c)

1382, 1247 cm^{-1} in FIG. 2a, 1373, 1224 cm^{-1} in FIG. 2b, and 1357, 1221 cm^{-1} in FIG. 2c, are assigned to the CH_3 symmetric deformation. The bands at 998, 1012 cm^{-1} , and 1011 cm^{-1} in FIG. 2a and 1357, 1221 cm^{-1} in FIG. 2c, are assigned to the CH_3 symmetric deformation. The bands at 990, 1012 cm^{-1} , and 1011 cm^{-1} in FIG. 2a through 2c, are all caused by the pyridine ring breathing vibration⁸. Comparing their relative intensity, we find that there is not obvious intensity change. This means that the pyridine ring stands up on the silver surface with a slope of certain degree. The difference of adsorbates on different silver surface can be differentiated by the band at 734 cm^{-1} in FIG. 2a and 732 cm^{-1} in FIG. 2b and FIG. 2c, which all are due to the out-of-plane C-H vibration. According to the "surface selection rules" by Moskovits and others^{9,10}, the vibration signals of adsorbed molecules, which had a component perpendicular to the surface, would be enhanced. The enhancing factor was directly proportional to the perpendicular component. In a random state corresponding to FIG. 2a, all molecular planes disorderly heap up. When adsorbed on silver surface, the molecules tend to range orderly. On the chemically reduced silver surface, in FIG. 2b, the band at 732 cm^{-1} , which is due to the out-of-plane C-H vibration in the pyridine ring, gained intensity. This suggests that the pyridine plane tend to stand up on the surface in very small slope, or in other words, that the pyridine plane tend to lie on the surface, shown as in FIG. 3a. Also this band at 734 cm^{-1} in FIG. 2a shifted to 732 cm^{-1} in FIG. 2c, and lost its intensity, but its intensity is stronger than that of in FIG. 2b after adsorbing. The decrease of intensity of 732 cm^{-1} band means that, on the HNO_3 etched silver surface the pyridine plane stands up on the surface in a large slope (see in FIG. 3b)

In the high wavenumber range, we can observe clear C-H vibration of the pyridine ring and C-H vibration of CH_3 at 3049 cm^{-1} and 2948 cm^{-1} in FIG. 2a, and at 3060 cm^{-1} , 2916 cm^{-1} in FIG. 2b. However we can not observe any corresponding bands due to C-H vibration in this range in FIG. 2c. Gi Xue and his co-workers also recorded the same results in the adsorption of 4-

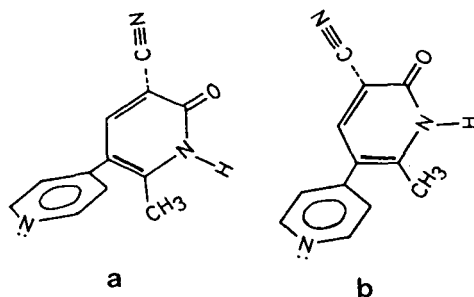


FIG. 3 Schematic diagram of adsorbed milrinone on chemically reduced silver surface (a) and on HNO_3 etched silver surface (b)

aminophenyl ammonium dithiocabate on the same substrates ⁶. This phenomenon perhaps is caused by the silver surface morphology. The silver surface, which is composed of chemically reduced silver particles, shows greater enhancing effect for the adsorbates than the HNO_3 etched silver surface.

CONCLUSION

The chemisorption of milrinone injection was recorded by Fourier transform Surface Enhanced Raman Scattering spectroscopy (FT-SERS). The results indicated that milrinone molecules tend to stand up on the HNO_3 etched silver surface with its pyridine plane, while it will lie on the chemically reduced silver film.

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